



⑪ Publication number : **0 390 044 B1**

⑫ **EUROPEAN PATENT SPECIFICATION**

④⑤ Date of publication of patent specification :  
**27.10.93 Bulletin 93/43**

⑤① Int. Cl.<sup>5</sup> : **B41M 5/38**

②① Application number : **90105731.5**

②② Date of filing : **26.03.90**

⑤④ **Heat transfer sheet.**

③① Priority : **28.03.89 JP 73745/89**  
**31.07.89 JP 196774/89**  
**26.10.89 JP 277106/89**

④③ Date of publication of application :  
**03.10.90 Bulletin 90/40**

④⑤ Publication of the grant of the patent :  
**27.10.93 Bulletin 93/43**

⑧④ Designated Contracting States :  
**DE FR GB**

⑤⑥ References cited :  
**EP-A- 0 245 836**  
**EP-A- 0 260 347**  
**EP-A- 0 304 673**  
**GB-A- 2 202 340**

⑤⑥ References cited :  
**PATENT ABSTRACTS OF JAPAN vol. 11, no.**  
**76 (M-569)(2523) 07 March 1987, JP-A-61**  
**230986**  
**PATENT ABSTRACTS OF JAPAN vol. 12, no.**  
**471 (M-773)(3318) 09 December 1988, JP-A-63**  
**194983**

⑦③ Proprietor : **DAI NIPPON INSATSU KABUSHIKI**  
**KAISHA**  
**1-1, Ichigaya-Kaga-Cho, Shinjuku-Ku**  
**Tokyo-To (JP)**

⑦② Inventor : **Egashira, Noritaka DAI NIPPON**  
**INSATSU KK**  
**1-1 Ichigaya Kaga-Cho 1-Chome**  
**Shinju-ku,Tokyo-T (JP)**

⑦④ Representative : **Müller-Boré & Partner**  
**Patentanwälte**  
**Isartorplatz 6 Postfach 26 02 47**  
**D-80059 München (DE)**

**EP 0 390 044 B1**

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

**Description****BACKGROUND OF THE INVENTION**

5 This invention relates to a heat transfer sheet, more particularly to a heat transfer sheet which is useful for the heat transfer system by use of a sublimable dye (heat migratable dye), excellent in dye migratability during heat transfer, and also can give excellent image density.

As the method for giving excellent monocolour or fullcolour image simply and at high speed in place of the impact printing or general printing method, non-impact printing such as the ink jet system or the heat transfer system has been developed. Among these, the so called sublimation heat transfer system by use of a sublimable dye is the most excellent as one having excellent continuous gradation and giving fullcolour image comparable with color photography.

10 The heat transfer sheet to be used in the sublimation type heat transfer system as mentioned above may be generally one having a dye layer comprising a sublimable dye and a binder formed on one surface of a substrate film such as polyester film, and a heat-resistant layer provided on the other surface of the substrate film for prevention of sticking of a thermal head.

By superposing the dye layer surface of such heat transfer sheet on an image receiving material having an image receiving layer comprising a polyester resin and like, and heating imagewise from the back of the heat transfer sheet by a thermal head, the dye in the dye layer is transferred to the image receiving material to form a desired image.

20 In the heat transfer system as described above, only the dye is migrated from the dye layer to the image receiving material, and the binder remains on the substrate film side. In this case, sharper and higher density image can be formed, as the migratability of the dye is better.

As the method for improving migratability of the dye, it is the simplest to increase printing energy, but higher printing energy results in increased printing cost undesirably. Further, when a plastic film is used as the substrate film, the thermal energy which can be applied is of itself limited.

As another method, it has been well known in the art to use a dye of low molecular weight, but when the molecular weight of the dye is low, there ensues the problem that fastness of the image formed such as bleed resistance, heat resistance is inferior.

30 As the method for circumventing such problems, the method of using a dye with a high molecular weight has been known. However, use of these dyes with high molecular weights involves the problem that migratability of the dye becomes inferior to form no sharp and high density image.

Accordingly, a first object of the present invention is to provide a heat transfer sheet which can form an image of satisfactory density with lower printing energy as compared with the prior art, or can form an image of higher density with the same printing energy as in the prior art.

35 Meanwhile, another known method for improving migratability of the dye to add a compound having low melting point such as wax, etc. as the sensitizer into the dye layer. However, addition of these low melting compounds gives rise to problems such as blocking of the heat transfer sheet wound up in a roll, bleeding of the dye to be transferred to the back, etc. Further, during heat transfer, there ensues the problem that the dye layer tends to be fused onto the surface of an image receiving material to be peeled off with difficulty. When it is peeled off, the dye layer tends to be migrated to the image receiving material.

40 An addition of fine particles such as silica as the release agent into the dye layer may be conceivable for solving these problems. However, in this case, the transferred image becomes coarse, whereby causing the problem that color reproducibility and resolution become low. Also, there is the method of adding a silicone oil as the release agent, but such silicone oil has no compatibility with the dye layer, whereby there are involved such problems as generation of surface stickiness, etc., occurrence of discoloration of the transferred image, whereby rather storability may be lowered.

45 Therefore, a second object of the present invention is to provide a heat transfer sheet which can form an image of satisfactory density with lower printing energy as compared with the prior art, or can form an image of higher density with the same printing energy as in the prior art without causing problems of storability and fusion to occur.

**SUMMARY OF THE INVENTION**

55 The object of the present invention is accomplished by the present invention as mentioned below.

That is, the present invention relates to a heat transfer sheet having a dye layer comprising a dye, a binder, sensitizer and a release agent provided on a substrate film, characterized in that said sensitizer is a low molecular weight substance having a melting point of 50 to 150°C, and the release agent is a graft copolymer

having at least one releasable segment selected from polysiloxane segments, fluorinated carbon segments and long chain alkyl segments graft-bonded to the main chain of the copolymer.

By permitting a sensitizer and a specific polymer release agent to exist in the dye layer, an image of satisfactory density can be formed with lower energy than the prior art without occurrence of problems of storability and fusion, and also, a heat transfer sheet capable of forming an image of further higher density and precision can be provided with the same printing energy as in the prior art.

#### DETAILED DESCRIPTION OF THE INVENTION

Referring now to preferred embodiments, the present invention is described in more detail.

The heat transfer sheet of the present invention comprises basically a dye layer formed on a substrate film similarly as in the prior art, but it is characterized by including a sensitizer and a specific release agent in said dye layer.

As the substrate film of the heat transfer sheet of the present invention as described above, any of those known in the art having heat resistance and strength to some extent may be available, as exemplified by papers, various converted papers, polyester films, polystyrene films, polypropylene films, polysulfone films, aramide films, polycarbonate films, polyvinyl alcohol films, Cellophane, etc. having a thickness of about 0.5 to 50  $\mu$ m, particularly preferably polyester films. These substrate films may be either in separated sheet form or continuous film, and not particularly limited. Among these, particularly preferable is a polyethylene terephthalate film with the surface previously subjected to easily adherable treatment.

The dye layer to be formed on the surface of the above-mentioned substrate film is a layer having at least a dye, a sensitizer and a release agent carried with any desired binder resin.

As the dye to be used, all of the dyes used in the heat transfer sheet known in the art are effectively available and not particularly limited. For example, some preferable dyes may include, as red dyes, MS Red G, Macrolex Red Violet R, Ceres Red 7B, Samaron Red HBSL, Resolin Red F3BS, etc., and also as yellow dyes, Foron Brilliant Yellow S-6GL, PTY-2, Macrolex Yellow 6G, etc., and also as blue dyes, Kayaset Blue 714, Waxoline Blue AP-FW, Foron Brilliant Blue S-R, MS Blue 100, etc.

As the binder resin for carrying the dye as mentioned above, any one of those known in the prior art can be used, and preferable examples may include cellulose resins such as ethyl cellulose, hydroxyethyl cellulose, ethylhydroxy cellulose, hydroxypropyl cellulose, methyl cellulose, cellulose diacetate, cellulose triacetate, cellulose acetate butyrate, etc.; vinyl resins such as polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl pyrrolidone, polyacrylamide, etc.; polyesters; and so on. Among them, cellulose type, acetal type, butyral type and polyester type, etc. are preferable from the points of heat resistance, migratability of dye, etc. Also, these binders should preferably have a Tg of 50°C or higher, because if Tg is lower than 50°C, the binder is liable to be softened when the sensitizer is melted during heat transfer, whereby the dye layer becomes readily fused to the image receiving material undesirably.

The sensitizer to be used in the present invention is a low molecular weight substance having a melting point of 50 to 150°C. If the melting point is lower than 50°C, the sensitizer will be readily migrated to the dye surface to generate such problem as blocking, etc., while if the melting point exceeds 150°C, the sensitizing action will be abruptly lowered undesirably.

The sensitizer to be used in the present invention should preferably have a molecular weight within the range of 100 to 1,500. If the molecular weight is less than 100, it is difficult to maintain the melting point at 50°C or higher, while if the molecular weight exceeds 1,500, sharpness of melting of the sensitizer during heat transfer is lost, whereby the sensitizing action becomes insufficient undesirably.

The above sensitizer should be used at a ratio of 1 to 100 parts by weight per 100 parts by weight of the binder forming the dye layer. If the amount used is less than 1 part by weight, it is difficult to obtain satisfactory sensitizing action, while if it exceeds 100 parts by weight, heat resistance of the dye layer will be lowered undesirably.

The sensitizer as described above may be any known low molecular substance, provided that it has a melting point of 50 to 150°C, but preferable sensitizers in the present invention may include thermoplastic resin oligomers, for example, various oligomers such as polyurethane oligomer, polystyrene oligomer, polyester oligomer, polyacryl oligomer, polyethylene oligomer, polyvinyl chloride oligomer, polyvinyl acetate oligomer, ethylene/vinyl acetate copolymer oligomer, ethylene-acryl copolymer oligomer, polyoxyethylene oligomer, polyoxypropylene oligomer, polyoxyethylenepropylene oligomer, etc.; fatty acids such as myristic acid, palmitic acid, malgaric acid, stearic acid, arachic acid, montanic acid, etc.; fatty acid amides such as caproic acid amide, caprylic acid amide, lauric acid amide, stearic acid amide, oleic acid amide, eicosenic acid amide, etc.; fatty acid esters such as methyl behenate, methyl lignocerate, methyl montanate, pentadecyl palmitate, hexacosyl stearate, carbamic acid [1,4-phenylenebis(methylene)]bisdimethyl ester, etc.; otherwise, aromatic compounds

such as 1,4-dicyclohexylbenzene, benzoic acid, aminobenzophenone, dimethyl terephthalate, fluoranthene, phenols, naphthalenes, phenoxys; various waxes; and so on.

The release agent to be used in the present invention is a polymer having at least one releasable segment, having releasable segments graft-bonded as the side chain to a polymer which is the main chain.

The releasable segment of such polymer itself is generally low in compatibility with the polymer as the main chain. Therefore, when the dye layer is formed by adding such polymer into the dye layer, or by use of the releasable polymer as the binder, the releasable segments are susceptible to microphase separation from the dye layer thereby to bleed out on the surface of the dye layer. On the other hand, the main chain tends to be integrated with the dye layer to adhere onto the substrate film. By concerting of these actions, the releasable segments are enriched on the surface side of the dye layer, whereby good releasability can be obtained. The releasable segments will not be departed from the dye layer with the main chain, and therefore they never migrated onto the surface of other articles such as image receiving material.

The above-mentioned releasable polymer is a graft copolymer having at least one releasable segment selected from polysiloxane segments, fluorinated carbon segments and long-chain alkyl segments graft-bonded to the main chain.

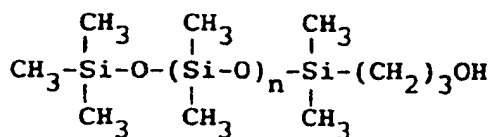
As the polymer of the main chain, any polymer having reactive functional group known in the art may be used. Preferable examples may include cellulose resins such as ethyl cellulose, hydroxyethyl cellulose, ethylhydroxy cellulose, hydroxypropyl cellulose, methyl cellulose, cellulose acetate, cellulose acetate butyrate, etc.; vinyl resins such as acrylic resin, polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl pyrrolidone, polyacrylamide, etc.; polyamide resins; polyurethane resins; polyester resins; and so on. Among these, from the point of compatibility with the binder, acrylic, vinyl, polyester, polyurethane, polyamide or cellulose resins are particularly preferred.

The above-mentioned releasable copolymer can be synthesized according to various methods. As a preferable method, the method of reacting a releasable compound having a functional group reactive with the functional group existing in the main chain after formation of said main chain may be employed.

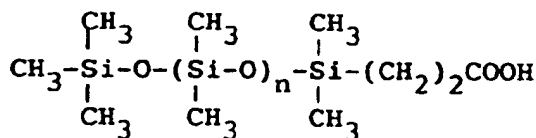
As an example of the releasable compound having the above-mentioned functional group, the compounds as set forth below may be included.

(a) Polysiloxane compounds:

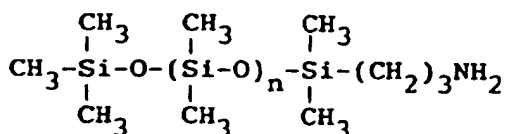
(1)



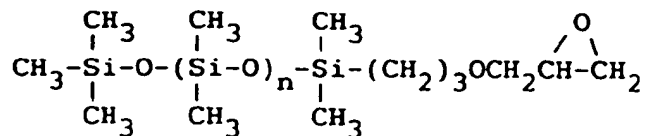
(2)



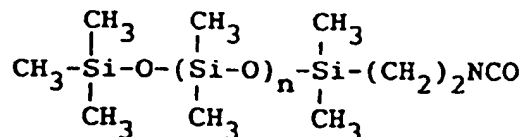
(3)



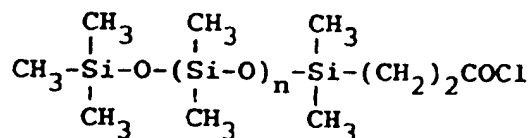
(4)



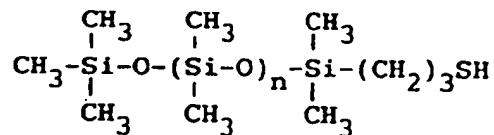
(5)



(6)



(7)



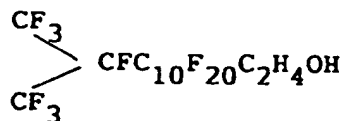
In the above formulae, a part of methyl groups may be also substituted with other alkyl groups or aromatic groups such as phenyl group, etc.

(b) Fluorinated carbon compounds:

(8)  $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{OH}$

(9)  $\text{C}_8\text{F}_{13}\text{C}_2\text{H}_4\text{OH}$

(10)



(11)  $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{OH}$

(12)  $\text{C}_{10}\text{F}_{21}\text{C}_2\text{H}_4\text{OH}$

(13)  $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{OH}$

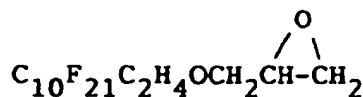
(14)  $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{OH}$

(15)  $\text{C}_8\text{F}_{13}\text{COOH}$

(16)  $\text{C}_8\text{F}_{13}\text{COCl}$

(17)  $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{SH}$

(18)



(c) Long-chain alkyl compounds:

Higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, etc. and acid halides thereof; higher alcohols such as nonyl alcohol, capryl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, linoleyl alcohol, ricinoleyl alcohol, etc.; higher aldehydes such as capric aldehyde, lauric aldehyde, myristic aldehyde, stearic aldehyde, etc.; higher amines such as decylamine, laurylamine, cetylamine, etc.

The above examples are merely illustrative, and other various reactive releasable compounds are available from, for example, Shinetsu Kagaku K.K., Japan, etc. and all of them can be used in the present invention. Particularly preferable is a mono-functional releasable compound having one functional group in one molecule, and when a polyfunctional compound having two or more functionalities is used, the graft copolymer obtained tends to be gelled undesirably.

The relationship of the above-mentioned functional releasable compound and the main chain polymer as illustrated above may be as shown below in Table B1, when the functional group of the releasable compound is represented by X and the functional group of the main chain polymer by Y. Of course, the relationship between X and Y may be vice versa, or the respective groups may be used in mixtures, and also these examples are not limitative, so long as both are reactive with each other.

Table B1

X	Y
-NCO	-OH, -NH <sub>2</sub> , -NHR-, -COOH, -SH, etc.
-COCl	-OH, -NH <sub>2</sub> , -NHR-, -SH, etc.
$\begin{array}{c} \text{--CH--CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	-OH, -NH <sub>2</sub> , -COOH, etc.
$\begin{array}{c} \text{--C=C--} \\ \diagup \quad \diagdown \\ \text{O=C} \quad \text{C=O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	-OH, -NH <sub>2</sub> , -NHR-, -SH, etc.
-OH, -SH	$\begin{array}{c} \text{--C=C--} \\ \diagup \quad \diagdown \\ \text{O=C} \quad \text{C=O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}, \text{--NCO, --COOR, --CHO, --COCl, --COOH, etc.}$
-NH <sub>2</sub> , -NHR-	$\begin{array}{c} \text{--C=C--} \\ \diagup \quad \diagdown \\ \text{O=C} \quad \text{C=O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}, \text{--NCO, --COOH, --COCl, --CH--CH}_2, \text{etc.}$
-COOH	$\begin{array}{c} \text{--CH--CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array}, \text{--NCO, --OH, --NH}_2, \text{--NHR--}, \text{etc.}$

As another preferable preparation method, also by reacting the above-mentioned functional releasable compound with a vinyl compound having a functional group reactive with the functional group to form a monomer having a releasable segment, and copolymerizing this with various vinyl monomers, a desired graft copolymer can be similarly obtained.

As another preferable preparation method, there may be employed the method in which a mercapto compound such as the above exemplary compound (7) or a releasable vinyl compound as mentioned above is added to a polymer having unsaturated double bond in its main chain such as unsaturated polyester, copolymer of vinyl monomer with a diene compound such as butadiene, etc. to be grafted thereon.

The above methods are preferable examples of preparation methods, and the present invention can also use graft copolymers prepared by other methods as a matter of course.

The content of the releasable segments in the above-mentioned polymer may be preferably within the range of the amount of the releasable segments occupied in the polymer ranging from 3 to 60 % by weight. If the amount of the releasable segments is too small, releasability becomes insufficient, while if it is too much, compatibility with the binder or the coating strength of the dye layer is lowered, and also the problem of discoloration or storability of the transferred image will occur undesirably.

The releasable polymer as described above can be also used as the binder in place of the above-described

binder.

The heat transfer sheet of the present invention can be obtained by coating and drying a solution of the dye, the sensitizer, the release agent and the binder as described above with addition of necessary additives dissolved in an appropriate organic solvent or at dispersion thereof in an organic solvent or water on at least one surface of the above-mentioned substrate film by formation means such as the gravure printing method, the screen printing method, the reverse roll coating method by use of gravure plate, etc. thereby forming a dye layer.

The dye layer thus formed has a thickness of about 0.2 to 5.0  $\mu$ m, preferably 0.4 to 2.0  $\mu$ m, and the sublimable dye in the dye layer should exist suitably in an amount of 5 to 90 % by weight, preferably 10 to 70 % by weight, of the weight of the dye layer.

The dye layer to be formed, when the desired image is mono-color, is formed by selecting one color from among the above-mentioned dyes, while when the desired image is a full-color image, for example, appropriate cyan, magenta and yellow (further black, if necessary) are selected to form a dye layer of yellow, magenta and cyan (and further black, if necessary).

According to the present invention as described above, by adding a sensitizer and a specific release agent into the dye layer, a heat transfer sheet which can form an image of satisfactory density with lower printing energy as compared with the prior art or can form an image of further higher density with the same energy as in the prior art without causing the problems of storability and fusion to occur can be obtained.

The present invention is described in more detail by referring to Examples and Comparative Examples. In the sentences, parts or % are based on weight, unless otherwise particularly noted.

#### Reference Example B1

40 Parts of a copolymer of 95 mole % of methyl methacrylate and 5 mole % of hydroxyethyl methacrylate (molecular weight 120,000) were dissolved in 400 parts of a solvent mixture of equal amounts of methyl ethyl ketone and toluene, and subsequently 10 parts of the polysiloxane compound (5) as exemplified above (molecular weight 3,000) were added dropwise gradually to carry out the reaction at 60°C for 5 hours.

The product was found to be uniform, and no polysiloxane compound could be separated by the fractional precipitation method, indicating that it was the reaction product of the polysiloxane compound and the acrylic resin. By analysis, the amount of the polysiloxane segments was about 7.4 %.

#### Reference Example B2

50 Parts of a polyvinyl butyral (polymerization degree 1,700, hydroxyl content 33 mole %) were dissolved in 500 parts of a solvent mixture of equal amounts of methyl ethyl ketone and toluene, and subsequently 10 parts of the polysiloxane compound (5) as exemplified above (molecular weight 3,000) were added dropwise gradually to carry out the reaction at 60°C for 5 hours.

The product was found to be uniform, and no polysiloxane compound could be separated by the fractional precipitation method, indicating that it was the reaction product of the polysiloxane compound and the polyvinyl butyral resin. By analysis, the amount of the polysiloxane segments was about 5.2 %.

#### Reference Example B3

70 Parts of a copolymer comprising 45 mole % of dimethyl terephthalate, 5 mole % of dimethyl monoa-minoterephthalate and 50 mole % of trimethylene glycol (molecular weight 25,000) were dissolved in 700 parts of a solvent mixture of equal amounts of methyl ethyl ketone and toluene, and subsequently 10 parts of the polysiloxane compound (4) as exemplified above (molecular weight 10,000) were added dropwise gradually to carry out the reaction at 60°C for 5 hours.

The product was found to be uniform, and no polysiloxane compound could be separated by the fractional precipitation method, indicating that it was the reaction product of the polysiloxane compound and the polyester resin. By analysis, the amount of the polysiloxane segments was about 5.4 %.

#### Reference Example B4

80 Parts of a polyurethane resin obtained from a polyethylene adipate diol, butane diol and hexamethylene diisocyanate (molecular weight 6,000) were dissolved in 800 parts of a solvent mixture of equal amounts of methyl ethyl ketone and toluene, and subsequently 10 parts of the polysiloxane compound (6) as exemplified above (molecular weight 2,000) were added dropwise gradually to carry out the reaction at 60°C for 5 hours.



The product was found to be uniform, and no polysiloxane compound could be separated by the fractional precipitation method, indicating that it was the reaction product of the polysiloxane compound and the polyurethane resin. By analysis, the amount of the polysiloxane segments was about 4.0 %.

#### Reference Example B5

100 Parts of a mixture of 5 mole % of the monomer obtained by the reaction of the above-mentioned polysiloxane compound (3) (molecular weight 1,000) with methacrylic acid chloride at a molar ratio of 1:1, 45 mole % of methyl methacrylate, 40 mole % of butyl acrylate and 10 mole % of styrene and 3 parts of azobisisobutyronitrile were dissolved in 1000 parts of a solvent mixture of equal amounts of methyl ethyl ketone and toluene, and polymerization was carried out at 70°C for 6 hours to obtain a viscous polymer solution.

The product was found to be uniform, and no polysiloxane compound could be separated by the fractional precipitation method. By analysis, the amount of the polysiloxane segments was about 6.1 %.

#### Reference Example B6

50 Parts of a styrene-butadiene copolymer (molecular weight 150,000, butadiene 10 mole %) and 2 parts of azobisisobutyronitrile were dissolved in 500 parts of a solvent mixture of equal amounts of methyl ethyl ketone and toluene, and subsequently 10 parts of the polysiloxane compound (7) as exemplified (molecular weight 10,000) were added dropwise gradually to carry out the reaction at 60°C for 5 hours.

The product was found to be uniform, and no polysiloxane compound could be separated by the fractional precipitation method, indicating that it was the reaction product of the polysiloxane compound and the copolymer. By analysis, the amount of the polysiloxane segments was about 6.2 %.

#### Reference Example B7

80 Parts of a hydroxyethyl cellulose were dissolved in 800 parts of a solvent mixture of equal amounts of methyl ethyl ketone and toluene, and subsequently 10 parts of the polysiloxane compound (6) (molecular weight 2,000) were added dropwise gradually to carry out the reaction at 60°C for 5 hours.

The product was found to be uniform, and no polysiloxane compound could be separated by the fractional precipitation method, indicating that it was the reaction product of the polysiloxane compound and the hydroxyethyl cellulose. By analysis, the amount of the polysiloxane segments was about 5.8 %.

#### Reference Example B8

A releasable graft copolymer was obtained in the same manner as in Reference Example B1 except for using the fluorinated carbon compound (16) as exemplified above in place of the polysiloxane compound in Reference Example B1.

#### Reference Example B9

A releasable graft copolymer was obtained in the same manner as in Reference Example B2 except for using the fluorinated carbon compound (18) as exemplified above in place of the polysiloxane compound in Reference Example B2.

#### Reference Example B10

A releasable graft copolymer was obtained in the same manner as in Reference Example B5 except for using methacrylate of the fluorinated carbon compound (10) as exemplified above in place of the polysiloxane compound in Reference Example B5.

#### Example B and Comparative Example B

On the surface of a polyethylene terephthalate film with a thickness of 6  $\mu$ m as the substrate applied with the heat-resistant treatment on the back opposite to the surface on which a dye layer is to be formed, an ink composition for formation of dye layer having the composition shown below was coated and dried by gravure printing to a thickness on drying of 1.0 g/m<sup>2</sup> to prepare heat transfer sheets of the present invention and Comparative Example shaped in continuous films.

**Kayaset Blue 714**

(Nippon Kayaku K.K., Japan, 5.50 parts  
C.I. Solvent Blue 63)

**Polyvinyl butyral resin**

(Ethlec BX-1, Sekisui Kagaku 3.00 parts  
Kogyo K.K., Japan)

Sensitizer (shown below in 1.00 part  
Table B2)

**Release agent (above**

Reference example) 1.00 part

Methyl ethyl ketone 22.54 parts

Toluene 68.18 parts

Next, by use of a synthetic paper (Oji-Yuka, Yupo FPG 150) as the substrate film, on one surface thereof was coated a coating solution having the following composition at a ratio of 4,5 g/m<sup>2</sup> on drying, followed by drying at 100°C for 30 minutes, to obtain image receiving materials to be used in the present invention and Comparative Example.

Polyester resin 11.5 parts

(Toyobo, K.K., Japan, Vylon 200)

**Vinylchloride-vinyl acetate  
copolymer**

(UCC, VYHH) 5.0 parts

**Amino-modified silicone oil**

(Shinetsu Kagaku Kogyo K.K., 1.2 parts  
Japan, KF393)

**Epoxy-modified silicone oil**

(Shinetsu Kagaku Kogyo K.K., 1.2 parts  
Japan, X-22-343)

Methyl ethyl ketone 40.8 parts

Toluene 40.8 parts

Cyclohexane 20.4 parts

**Heat transfer test**

Each of the heat transfer sheet of the above-mentioned Example B and Comparative Example B and the image receiving material as described above were superposed as opposed to each other, and by use of a thermal head (KMT-85-6, MPD2) from the back of the heat transfer sheet, thermal head recording was performed under the condition of a head application voltage of 12.0 V, step pattern successively reduced at every 1 msec. from applied pulse width of 16.0 msec./line, and 6 line/mm (33.3 msec./line) in the sub-scanning direction to give the results shown below in Table B2.

Table B2

Example	Sensitizer	Release agent	Releasability	Relative sensitivity
B1	Polystyrene oligomer (mp=60°C, mw=860)	Reference Example B1	○	1.4
B2	Polyoxyethylene oligomer (mp=50°C, mw=900)	Reference Example B2	○	1.3
B3	Eiconsenic acid amide (mp=79°C, mw=310)	Reference Example B3	○	1.9
B4	Carbamic acid [1,4-phenylenebis(methylene)] bisdimethylester (mp=95°C, mw=252)	Reference Example B4	○	1.5
B5	1,4-Dicyclohexylbenzene (mp=100°C, mw=218)	Reference Example B5	○	1.3
B6	Fluoranthene (mp=110°C, mw=202)	Reference Example B6	○	1.4
B7	Benzoic acid (mp=122.5°C, mw=122)	Reference Example B7	○	1.3
B8	o-Aminobenzophenone (mp=110°C, mw=197)	Reference Example B8	○	1.4
B9	Dimethyl terephthalate (mp=142°C, mw=194)	Reference Example B9	○	1.3
B10	Lauric acid amide (mp=100°C, mw=199)	Reference Example B10	○	1.4
Comparative Example				
B1	No sensitizer (binder was made 4.0 parts)	Reference Example B1	○	1.0
B2	Polyoxyethylene oligomer (mp=50°C, mw=900)	NO release agent (binder was made 4.0 parts)	x	1.3

The relative sensitivity was determined by measuring the printed image density and comparing it relatively with the printing density of Comparative example A1 as 1.0, and releasability was judged by peeling off the

h at transfer sheet after printing:

○ : easily peeled off without problem

× : peeled off with difficulty with a part of the dye layer transferred as such.

- 5 As described above, according to the present invention, the density improvement effect by 30 % or more was obtained with the same printing energy by adding only a specific sensitizer and a release agent into the dye layer.

## 10 Claims

1. A heat transfer sheet having a dye layer comprising a sublimable dye, a binder, a sensitizer and a release agent, provided on a substrate film,  
said sensitizer being a low molecular weight substance having a melting point of 50 to 150°C;  
15 said release agent being a graft copolymer having at least one releasable segment selected from polysiloxane segments, fluorinated carbon segments and long chain alkyl segments graft-bonded to the main chain of the copolymer; and wherein  
said release agent can be used alternatively as said binder in place of said binder.
- 20 2. A heat transfer sheet according to claim 1, wherein the main chain of the releasable polymer is compatible with the binder.
3. A heat transfer sheet according to claim 1 or 2, wherein the main chain of the releasable polymer is an acrylic, vinyl, polyester, polyurethane, polyamide or cellulose resin.
- 25 4. A heat transfer sheet according to any one of claims 1 to 3, wherein the low molecular weight substance has a molecular weight of 100 to 1,500.
5. A heat transfer sheet according to any one of claim 1 to 4, wherein the amount of the low molecular weight substance is 1 to 100 parts by weight per 100 parts by weight of the binder.
- 30 6. A heat transfer sheet according to any one of claim 1 to 5, wherein the binder has a Tg of 50°C or higher.
7. A heat transfer sheet according to any one of claim 1 to 6, wherein the surface of the substrate sheet is subjected to easy adhesion treatment.

35

## Patentansprüche

1. Wärmeübertragungsfolie mit einer Farbstoffschicht, die einen sublimierbaren Farbstoff, ein Bindemittel, einen Sensibilisator und ein Freisetzungsmittel aufweist und auf einem Substratfilm vorgesehen ist,  
welcher Sensibilisator eine Substanz mit niedrigem Molekulargewicht und einem Schmelzpunkt von 50 bis 150°C ist;  
welches Freisetzungsmittel ein Pfropfcopolymer mit mindestens einem freisetzbaren Segment ist,  
das aus Polysiloxansegmenten, fluorierten Kohlenstoffsegmenten und langkettigen Alkylsegmenten, die  
45 zur Hauptkette des Copolymers pfropfgebunden sind, ausgewählt ist; und worin  
das Freisetzungsmittel alternativ als das Bindemittel anstelle des Bindemittels verwendet werden kann.
2. Wärmeübertragungsfolie nach Anspruch 1, worin die Hauptkette des freisetzbaren Polymers mit dem Bindemittel kompatibel ist.
3. Wärmeübertragungsfolie nach Anspruch 1 oder 2, worin die Hauptkette des freisetzbaren Polymers ein Acryl-, Vinyl-, Polyester-, Polyurethan-, Polyamid- oder Celluloseharz ist.
4. Wärmeübertragungsfolie nach irgendeinem der Ansprüche 1 bis 3, worin die Substanz mit dem niedrigen Molekulargewicht ein Molekulargewicht von 100 bis 1.500 besitzt.
5. Wärmeübertragungsfolie nach irgendeinem der Ansprüche 1 bis 4, worin die Menge der Substanz mit dem niedrigen Molekulargewicht 1 bis 100 Gewichtsteile pro 100 Gewichtsteile Bindemittel ist.

55

6. Wärmeübertragungsfolie nach irgendeinem der Ansprüche 1 bis 5, worin das Bindemittel eine Tg von 50°C oder höher besitzt.
- 5 7. Wärmeübertragungsfolie nach irgendeinem der Ansprüche 1 bis 6, worin die Oberfläche der Substratfolie in r Behandlung zum mühelosen Haften unterzogen ist.

# Revendications

10

1. Feuille pour le transfert de chaleur ayant une couche de colorant comprenant un colorant sublimable, un liant, un sensibilisateur et un agent de libération, fournis sur un film substrat, ledit sensibilisateur étant une substance de faible masse moléculaire ayant un point de fusion de 50 à 150°C;

15

ledit agent de libération étant un copolymère greffé ayant au moins un segment libérable choisi parmi les segments polysiloxane, les segments de carbone fluoré et les segments alkyle à longue chaîne liés par greffage à la chaîne principale du copolymère; et dans laquelle on peut utiliser, en variante, ledit agent de libération en tant que ledit liant au lieu dudit liant.

20

2. Feuille pour le transfert de chaleur selon la revendication 1, dans laquelle la chaîne principale du polymère libérable est compatible avec le liant.

3. Feuille pour le transfert de chaleur selon la revendication 1 ou 2, dans laquelle la chaîne principale du polymère libérable est une résine acrylique, vinylique, polyester, polyuréthane, polyamide ou cellulosique.

25

4. Feuille pour le transfert de chaleur selon l'une quelconque des revendications 1 à 3, dans laquelle la substance de faible masse moléculaire a une masse moléculaire de 100 à 1 500.

30

5. Feuille pour le transfert de chaleur selon l'une quelconque des revendications 1 à 4, dans laquelle la quantité de substance de faible masse moléculaire est de 1 à 100 parties en poids pour 100 parties en poids du liant.

6. Feuille pour le transfert de chaleur selon l'une quelconque des revendications 1 à 5, dans laquelle le liant a une T<sub>v</sub> de 50°C ou supérieure.

35

7. Feuille pour le transfert de chaleur selon l'une quelconque des revendications 1 à 6, dans laquelle la surface de la feuille de substrat est soumise à un traitement d'adhérence facile.

40

45

50

55